

Electrically tunable quantum anomalous Hall effect in 5d transition-metal adatoms on graphene

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The combination of the unique properties of graphene with spin polarization and magnetism for the design of new spintronic concepts and devices has been hampered by the small Coulomb interaction and the tiny spin-orbit coupling of carbon in pristine graphene. Such device concepts would take advantage of the control of the spin degree of freedom utilizing the widely available electric fields in electronics or of topological transport mechanisms such as the conjectured quantum anomalous Hall effect. Here we show, using first-principles methods, that 5d transition-metal (TM) adatoms deposited on graphene display remarkable magnetic properties. All considered TM adatoms possess significant spin moments with colossal magnetocrystalline anisotropy energies as large as 50 meV per TM atom. We reveal that the magneto-electric response of deposited TM atoms is extremely strong and in some cases offers even the possibility to switch the spontaneous magnetization direction by a moderate external electric field. We predict that an electrically tunable quantum anomalous Hall effect can be observed in this type of hybrid materials.

Spin-orbit interaction, which couples the spin degree of freedom of electrons to their orbital motion in the lattice, leads to many prominent physical phenomena, such as the antisymmetric exchange interaction [1], the colossal magnetic anisotropy [2], or the anomalous Hall effect [3] in conventional ferromagnets. It is also the key interaction in the newly-found quantum topological phase in topological insulators, where the quantum spin Hall effect was observed experimentally [4], and the quantum anomalous Hall effect (QAHE) was predicted to exist [5, 6]. Since the orbital motion can be manipulated with external electric fields, spin-orbit coupling (SOC) opens a route to dissipationless transport and to electrical control of magnetic properties [7–9], playing a crucial role in future spintronics applications.

Owing to its strong spin-orbit coupling, heavy 4d and 5d TMs display fascinating physical properties for desirable spintronic applications, especially when combined with non-vanishing magnetization. However, magnetism of 5d TMs proved difficult to achieve due to their more delocalized valence d wavefunctions and the smaller intra-atomic exchange integrals compared to 3d TMs such as Fe, Co, or Ni. Low-dimensional structures, such as monolayers [10], atomic wires [11], and clusters [12], were proposed to facilitate the stability of 5d magnetism by reducing the d - d hybridization. Nevertheless, when deposited on substrates of noble or late transition metals, such as Cu, Ag, Au, and Pt, interdiffusion at interfaces is inevitable, and strong hybridization between the d states of the substrate and of the adatoms is also destructive for 5d magnetism. From this point of view, using sp substrates is more promising. In fact, 4d ferromagnetism was first observed in a Ru monolayer deposited on the graphite (0001) surface [13], which is close in its chemical and physical properties to graphene.

Since the day graphene was isolated and produced as a two-dimensional material [14], it abruptly altered the research direction of material science [15] with the aim of exploring its fascinating transport properties. In a sense, graphene serves as a prototype of topological insulators [16]. For instance, the Berry phase of π of electronic states in graphene induces a half-integer quantum Hall effect [17, 18], while the existence of the quantum spin Hall effect was first suggested for pure graphene when SOC is taken into account [19]. One common feature for those transport properties is the non-trivial topological origin, resulting in dissipationless charge or spin current carried by edge states with conductivity quantized in units of e^2/h . However, from the application point of view, a large external magnetic field is required to obtain the quantum Hall effect, and the spin-degeneracy in the quantum spin Hall effect makes it hard to manipulate the spin degree of freedom by controlling external fields. To avoid such constraints while keeping the benefit of topologically protected quantized topological transport, the long-sought QAHE is a perfect solution. The essence of the QAHE lies in the quantization of the transverse charge conductivity in a material with intrinsic non-vanishing magnetization. The fact that the magnetization in ferromagnets can be much easier handled experimentally than large magnetic fields makes the QAHE extremely attractive for applications in spintronics and quantum information. However, at present the QAHE is merely a generic theoretical concept for magnetically doped topological insulators [5, 6]. Recently, Qiao *et al.* suggested that the QAHE could also occur at comparatively low temperatures in graphene decorated with Fe adatoms [20].

Here, we demonstrate based on first-principles theory that 5d TMs deposited on graphene are strongly mag-

netic, provide colossal magneto-crystalline anisotropy energies and exhibit topologically non-trivial band gaps due to very strong spin-orbit interaction. A generic representative of this hybrid class of materials has a magneto-crystalline anisotropy energy of 10–30 meV per TM and a quantum anomalous Hall gap in its electronic spectrum with the size of 20–80 meV. In connection with a large magneto-electric response of the deposited adatoms, we predict that within this class of systems an electrically tunable QAHE at room temperature could be achieved experimentally.

We have performed first-principles calculations of 5d TM (Hf, Ta, W, Re, Os, Ir, and Pt) adatoms on graphene in 2×2 , 3×3 , and 4×4 supercell geometries corresponding to the deposition density of 4.7, 2.1 and 1.2 atoms/nm², respectively (see the Method part for details). Throughout this work the TM atoms are placed at the hollow sites of graphene. According to previous theoretical studies [21], it is the most favorable absorption site with the exceptions of Pt [22] and Ir [23], for which the bridge site is more preferable. Among all systems studied we selected one prototype system, W on graphene, that we discuss in more detail. In the 4×4 geometry, the optimized distance between W adatoms on the hollow site and the C plane is about 1.74 Å, and the hollow site is about 0.14 eV (0.41 eV) per TM atom lower in energy than the bridge (top) site, in agreement with previous observations [24]. Applying an electric field, the relaxed positions change by at most 0.01 Bohr radii, and the hollow site remains the preferred adsorption site.

Turning now to magnetism, and looking first at TM atoms adsorbed in the 4×4 supercell, we find that most of the 5d TM atoms (except for Pt) are magnetic with sizable magnetic moments (see Fig. 1a) ranging between 0.5 and $2\mu_B$. This is consistent with the large magnetization energy calculated, defined as the total energy difference between the nonmagnetic and ferromagnetic state, reaching e.g. for Ta and W values as high as 0.56 eV and 0.34 eV, respectively. Surprisingly, the magnetic moments across the series of the rather isolated TM atoms do not follow Hund's first rule, i.e. the magnetic moments do not increase in steps of $1\mu_B$ from Hf to Re, reaching a maximum at the center of the TM series and decreasing again from Re to Pt. On the contrary we find the minimal spin moment for Re. This demonstrates the role of the hybridization of the TM *d*-orbitals with graphene. Increasing the deposition density studying a 3×3 supercell, the results remain basically unaltered, indicating that the *d-d* hybridization between neighboring adatoms is weak and that the physics is determined by the local TM-graphene bonding. This changes in the case of the 2×2 geometry, when the adatoms are in close vicinity to each other and the magnetism survives only for Ta, W, Re, and Ir atoms.

Unique to the 5d TMs is the property that the SOC and the intra-atomic exchange are of the same magnitude.

From this we anticipate a significant influence of SOC on the electronic properties, leading to strong anisotropies of the calculated quantities upon changing the direction of magnetization \mathbf{M} relative to the graphene plane.

The most impressive manifestation of SOC in the TM-graphene hybrid materials are the colossal values of the magneto-crystalline anisotropy energy (MAE), defined as the total-energy difference between the magnetic states with spin moments aligned in the plane and out of the graphene plane. The MAE presents one of the most fundamental quantities of any magnetic system as its sign defines the easy magnetization axis and its magnitude gives an estimate on the stability of the magnetization with respect to temperature fluctuations – a key issue for magnetic storage materials. A large MAE makes the magnetization very stable but also difficult to manipulate.

The values of the MAE obtained in 3×3 and 4×4 geometry, presented in Fig. 1b, lie in the range of 10 to 50 meV per TM. These are orders of magnitude larger than the values for 3d TMs, irrespective of whether they are arranged in bulk, thin films or multilayers. Similar colossal MAE magnitude has been reported for the free-standing 4d and 5d TM chains [11] as well as dimers of TMs [25]. Characteristic for the colossal MAE [2] is the significant contribution from the variation of magnetic moments and corresponding magnetization energies when changing the direction of \mathbf{M} , a contribution that is absent for conventional 3d magnets. For instance, for 4×4 W on graphene, this variation of the spin moment reaches as much as $0.1\mu_B$ (Fig. 2a). By looking at the MAE values as the function of the band filling and deposition density in Fig. 2b, we find that, in contrast to the spin moments, the MAE exhibits a much more irregular behavior as a function of the band filling and depends much more sensitively on the adatom density. E.g. for W the MAE changes sign depending on the density of adatoms, and has a small value in the 4×4 geometry. Such a situation provides a possibility to manipulate the magnetization direction with weak external perturbations, which can be particularly important for transport applications as we demonstrate below.

In search for ability to manipulate the magnetic properties of adatoms by external fields, we show in Fig. 2 the dependence of the spin moments and the MAE of W adatoms in 4×4 geometry on the strength of the electric field \mathcal{E} , applied perpendicularly to the graphene layer (along the *z*-axis). Remarkably, the spin moment of W displays a strong dependence on the field strength, especially when the magnetization points out of plane. Qualitatively, this response can be characterized by a magnetoelectric coefficient α , which relates the change in the spin moment to the strength of the \mathcal{E} -field in the zero-field situation: $\mu_0\Delta\mu_S(W) = \alpha\mathcal{E}$, where μ_0 is the vacuum magnetic permeability constant. For 4×4 W on graphene and an out-of-plane magnetization, α_\perp amounts to about

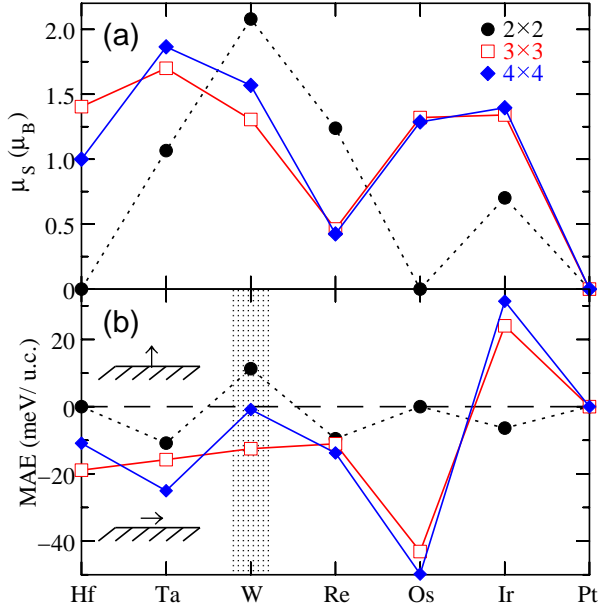


FIG. 1: Magnetic moments and MAE of 5d adatoms on graphene. (a) Magnetic moments due to electron spin, μ_S , calculated without SOC and (b) the MAE of 5d TM adatoms on graphene in 2×2 , 3×3 and 4×4 superlattice geometry. Positive (negative) values of MAE imply an out-of-plane (in-plane) easy axis of the spin moments, i.e. perpendicular to (in) the graphene plane.

$3 \cdot 10^{-13}$ G-cm²/V, which is one order of magnitude larger than that in Fe thin films [8]. For an in-plane magnetization, the magnetoelectric coefficient α_{\parallel} is only $6 \cdot 10^{-14}$ G-cm²/V, i.e. one order of magnitude smaller than α_{\perp} , which underlines the strong anisotropy of this quantity. We observe similarly large variations of the magnetoelectric coupling strength in other considered 5d TMs. The variation of orbital moment with varying \mathcal{E} -field is negligible for all systems.

Striking is the effect of the electric field on the magnetization direction (see Fig. 2b). At zero field ($\mathcal{E} = 0$) the magnetization is in-plane. Applying a negative field of magnitude of 0.05–0.4 V/Å, values typical in graphene field effect transistor structures [26], the sign of the MAE is changed. This means that the equilibrium direction of the magnetization can be switched from in-plane (MAE < 0, for $\mathcal{E} = 0$) to out-of-plane (MAE > 0 for $\mathcal{E} < 0$). Supposing that the \mathcal{E} -field is completely screened in our system by forming a screening charge δq , the variation of the MAE with respect to δq , $\delta \text{MAE}/\delta q$, reaches as much as 28 meV/e for negative electric fields, which is more than three times larger than that on the surface of CoPt slabs [27], and one order of magnitude larger than that of Fe slabs [8]. With a moderate out-of-plane electric field of ± 0.13 V/Å switching of the magnetization can be also achieved in 4×4 Hf, and the MAE can be significantly altered in 4×4 Os on graphene (by ≈ 10 meV)

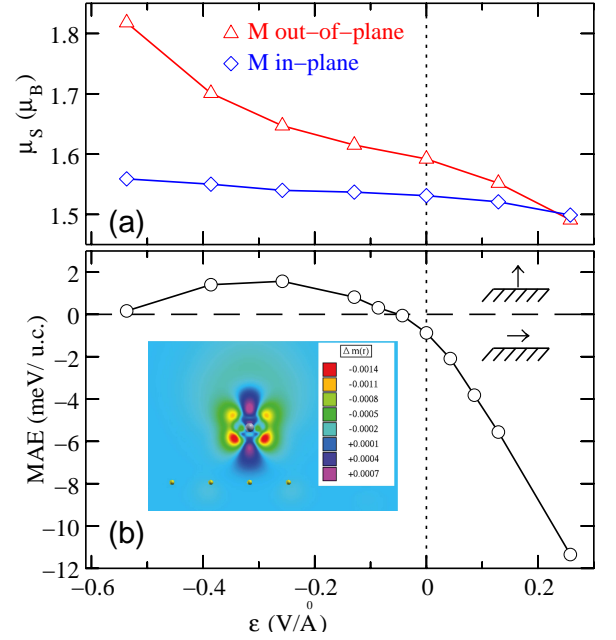


FIG. 2: Dependence of the magnetic moments (a) and magnetic anisotropy energy MAE (b) of 4×4 W on graphene on the strength of an external electric field. (a) The spin moment of W adatoms μ_S (in μ_B) as a function of the strength of an external electric field \mathcal{E} , perpendicular to graphene surface, for the out-of-plane and in-plane magnetization, respectively. Negative values of \mathcal{E} correspond to the electric field in $+z$ -direction, i.e. the direction from graphene towards the adatoms. (b) Dependence of the MAE on the strength of an external electric field \mathcal{E} , sign convention of MAE is consistent to Fig. 1. Inset displays the difference of spin densities $\Delta m(r)$ for the system without electric field and the case with a negative electric field of 0.13 V/Å.

and 4×4 Ir on graphene (by ≈ 20 meV). This establishes 5d TM adatoms on graphene as a class of magnetic hybrid materials with high susceptibility of magnetic properties to the electric field, thus making the electrical control of magnetism in these systems possible.

The reason for such a strong magnetoelectric response of 5d TMs on graphene can be exemplified for the case of W in 4×4 geometry. The local W s - and d -decomposed density of electron states without SOC, grouped into $\Delta_1(s, d_{z^2})$, $\Delta_3(d_{xz}, d_{yz})$ and $\Delta_4(d_{xy}, d_{x^2-y^2})$ contributions, is presented in Fig. 3a. As we can see, the W spin moment of about $1.6\mu_B$ originates from two occupied spin-up and two unoccupied spin-down Δ_1 -states, while the exchange-split Δ_3 - and Δ_4 -states are situated above and below E_F , respectively, and almost do not contribute. Upon including SOC (e.g. for out-of-plane spins) a strong hybridization between the Δ_1^{\downarrow} , and Δ_3 and Δ_4 states of both spin occurs around E_F (see also Fig. 3b), which results in a formation of hybrid bands of mixed spin and orbital character, while the Δ_1^{\uparrow} band remains mainly non-bonding (see Fig. 3c). When an elec-

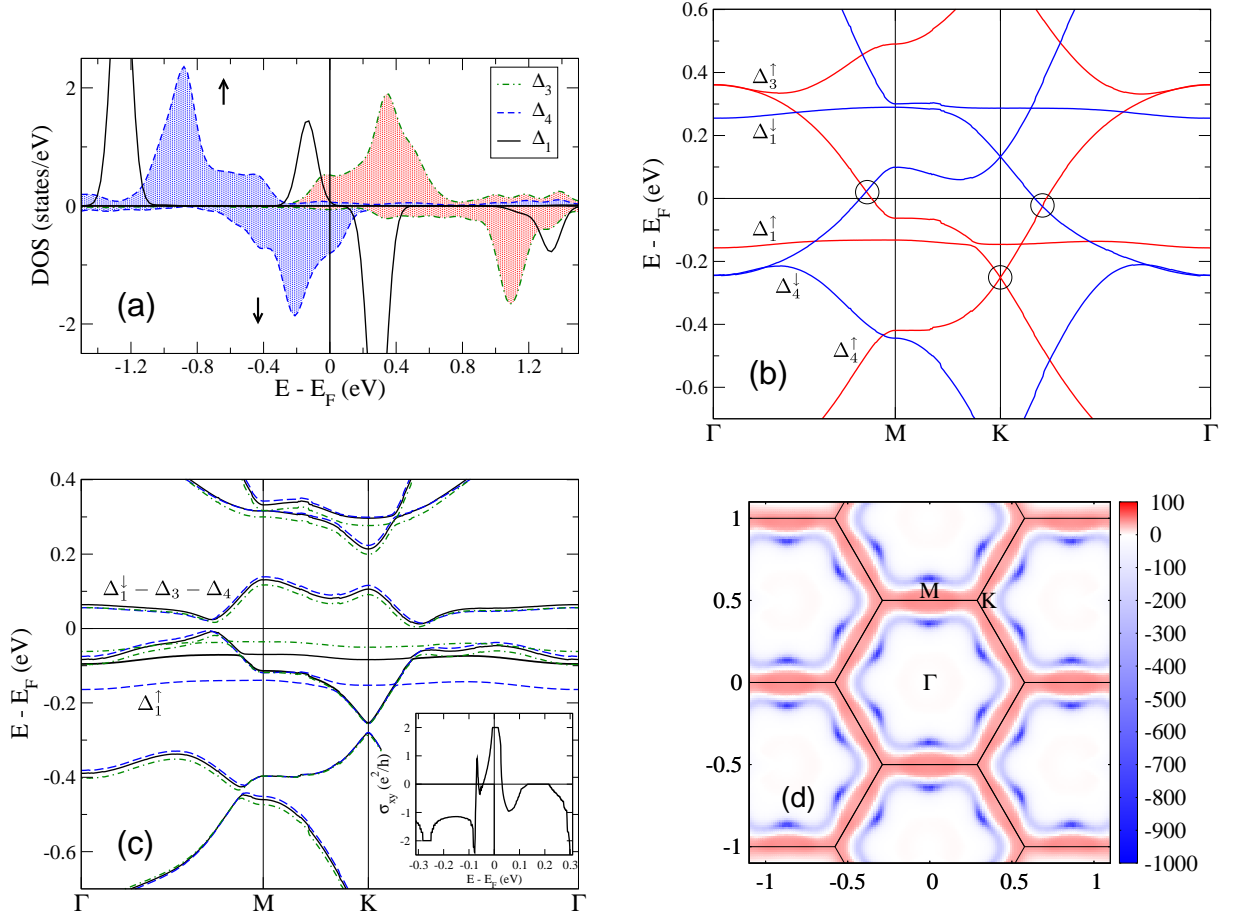


FIG. 3: Electronic structure of 4×4 W on graphene. (a) Density of $\Delta_1(s, d_{z^2})$, $\Delta_3(d_{xz}, d_{yz})$ and $\Delta_4(d_{xy}, d_{x^2-y^2})$ states without SOC. Up and down arrows mark spin-up and spin-down channels, respectively. (b) Band structure without SOC along high symmetry lines in the 2D Brillouin zone. Red and blue color of the bands stands for the spin-up and spin-down character, respectively. Circles highlight the points at which the gap will open when SOC is considered. (c) Band structures with SOC for $\mathbf{M} \parallel z$: without electric field (solid line), with positive (dashed) and negative (dot-dashed) electric field of the magnitude of 0.13 V/\AA . The inset shows the anomalous Hall conductivity of the system with respect to the position of the Fermi energy E_F for $\mathcal{E} = 0$ and $\mathbf{M} \parallel z$. (d) Berry curvature distribution of occupied bands in the momentum space (in units of $\frac{2\pi}{a}$, with a as the in-plane lattice constant of the 4×4 supercell). The Brillouin zone boundaries are marked with solid lines.

tric field is applied along the z -axis, the states which experience most influence of the corresponding potential change are the Δ_1^\uparrow -states, directed perpendicularly to the graphene plane. Corresponding modification of the band structures due to the electric fields can be seen in Fig. 3c, where the Δ_1^\uparrow band is shifted downwards (upwards) by negative (positive) applied \mathcal{E} fields, while the hybrid bands of mixed character remain almost unaffected. This causes the redistribution of the electrons in the Δ_1^\uparrow -states, its hybridization with the hybrid band below the Fermi level and hence the variation of the magnetic moment. This can be visualized by the plot of the spin density difference $\Delta m(\mathbf{r})$ for the case with $\mathcal{E} = 0$ and $\mathcal{E} = -0.13 \text{ V/\AA}$ (inset in Fig. 2b). It is obvious that, upon applying an electric field, a certain amount of spin density is transferred from the Δ_1 state of d_{z^2} character to the Δ_3 states. Owing to the difference in the hybridiza-

tion with the graphene states, seen from the width of the corresponding peaks in the density of states, the Δ_1 and Δ_3 states have different localization inside the W atoms thus leading to a change in the spin moment.

At last we turn to the prediction of a stable QAHE, a manifestation of the quantization of the transverse anomalous Hall conductivity. It is motivated by the observation that for 4×4 W on graphene with an out-of-plane magnetization, Δ_3 and Δ_4 bands of opposite spin cross (see circles in Fig. 3b) and hybridize under the presence of SOC, forming a global band gap across the Brillouin zone (BZ). Thus, 4×4 W becomes an insulator upon a spin-orbit driven metal-insulator transition. We compute the anomalous Hall conductivity of this system, given by $\sigma_{xy} = (e^2/h)\mathcal{C}$, with \mathcal{C} as the Chern number of all occupied bands that can be obtained as a k -space integral $\mathcal{C} = \frac{1}{2\pi} \int_{\text{BZ}} \Omega(\mathbf{k}) d^2k$. The integrand, $\Omega(\mathbf{k})$, is the

so-called Berry curvature of all states below the Fermi level:

$$\Omega(\mathbf{k}) = \sum_{n < E_F} \sum_{m \neq n} 2\text{Im} \frac{\langle \psi_{n\mathbf{k}} | v_x | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | v_y | \psi_{n\mathbf{k}} \rangle}{(\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}})^2}, \quad (1)$$

where $\psi_{n\mathbf{k}}$ is the spinor Bloch wavefunction of band n with corresponding eigen energy $\varepsilon_{n\mathbf{k}}$, v_i is the i 'th Cartesian component of the velocity operator. The Berry curvature in reciprocal space, presented in Fig. 3d, displays a comparatively complex pattern, with positive contributions concentrated along the BZ boundary, and large negative dips at certain isolated k -points away from the high-symmetry points. Such non-trivial distribution of the Berry curvature, which plays a role of an effective magnetic field in the k -space, is typical for complex transition-metal compounds [3].

The calculated anomalous Hall conductivity as a function of the electron filling expressed as energy E relative to the Fermi level is presented in the inset of Fig. 3c for an out-of-plane magnetization, $\mathbf{M}||z$, and zero \mathcal{E} -field. We indeed find that the Chern number of all occupied states acquires an integer value of $+2$. According to the physics of the quantum Hall effect, this will result in two dissipationless and topologically protected edge states on each side of a finite graphene ribbon with W adatoms. Remarkably, another 32 meV large QAHE gap with the $\mathcal{C} = -2$ can be observed at the energy of -0.27 eV below E_F , originating from the SOC-mediated hybridization between the Δ_3 and Δ_4 bands of the same spin-up character, see Figs. 3b and 3d. Such a peculiar situation suggests that the topological properties of the QAHE state in 4×4 W on graphene can be controlled by tuning the position of E_F e.g. via deposition on an appropriate substrate.

More importantly, at equilibrium the magnetization direction of 4×4 W lies in-plane, rendering $\sigma_{xy} = 0$ owing to the antisymmetric nature of the anomalous Hall conductivity with respect to the magnetization direction. From our previous observations it follows, however, that the direction of \mathbf{M} can be conveniently switched to out-of-plane by applying a moderate electric field without any significant modification of the electronic structure. The gaps remain intact (cf Fig. 3c), its size unchanged, and the value of the anomalous Hall conductivity remains quantized at both energies.

Such non-trivial topological QAHE states occur also for all other $5d$ adatoms (except Pt) on graphene in 4×4 geometry, and several of them in 2×2 geometry, with the QAHE gaps of comparable magnitude, although positioned away from the Fermi energy. For example, graphene with Re deposited in 4×4 geometry exhibits three $\mathcal{C} = +2$ QAHE gaps at -1 , -0.15 and $+0.67$ eV, with the corresponding gap size of 38, 63 and 98 meV, respectively. Also, 4×4 Ir and Os on graphene show two QAHE gaps ($\mathcal{C} = +2$ for Ir and $\mathcal{C} = \pm 2$ for Os) at 0.24

and 0.47 eV for Ir, and -0.38 and 0.15 eV for Os, with corresponding gap size in between 11 and 80 meV. The fact that several QAHE gaps with different Chern numbers at different energies can occur in the same material makes these systems a rich playground for topological transport studies. Characteristic of such systems is the leading role of the $5d$ orbitals and strong SOC of heavy adatoms in determining the topological properties: as we can see from Fig. 3b, the creation of the QAHE gaps can occur at the points in the Brillouin zone away from high-symmetry points due to hybridization of bands with a strong TM character, which are significantly altered by the TMs' SOC. This is in contrast to the cases considered previously [5, 6, 20], in which the role of the magnetic adatoms is rather to insert a Rashba spin-orbit or exchange fields on the Dirac states at the Fermi energy and high-symmetry points in the Brillouin zone. Most importantly, however, the strong SOC of $5d$ TMs leads to an increase of the QAHE gap by an order of magnitude, when compared to all QAHE systems suggested before, guaranteeing a strong topological protection against defects, structural disorder or thermal fluctuations, and thus opening a route to QAHE at room temperature.

To summarize, we predict that graphene decorated with $5d$ transition-metals is a hybrid material displaying remarkable magnetic and transport properties, which may be utilized experimentally for the purposes of topological transport applications at reasonable temperatures and conditions. The fact that heavy transition-metals deposited on graphene display very stable magnetism due to colossal magneto-crystalline anisotropies with exciting possibilities in engineering a robust quantum anomalous Hall effect with a large band gap stems from the strong spin-orbit interaction of these elements. The extreme sensitivity of these hybrid systems to an electric field that we predicted is likely to be enhanced when graphene is deposited on a ferroelectric substrate. Thus $5d$ -graphene hybrid materials provide a unique functionality in tailoring the required magnetic and topological properties, not likely to be achieved in conventional magnetic materials based on $3d$ transition-metals. Considering the breadth of this material class including other possible heavy adatoms, such as the $4d$ TMs or $4f$ -elements, we anticipate that room temperature QAHE may become possible in these systems and we encourage intense experimental research on these materials.

Method

The theoretical investigations are based on density functional theory [28], which is 'first-principles' in that it requires no experimental input other than the nuclear charges. We apply the generalized gradient approximation [29] to the exchange-correlation potential and use the full-potential linearized augmented plane

wave method (FLAPW) as implemented in the FLEUR code [30]. The self-consistent calculations with SOC were carried out with the cut-off parameter k_{max} of 4.0 bohr⁻¹ and 144 k -points (for the 4×4 cases) in the full two-dimensional Brillouin zone. The muffin-tin radius of 2.7 bohr (1.2 bohr) was used for TM (carbon) atoms. To calculate the transverse anomalous Hall conductivity accurately, we applied the Wannier interpolation technique, using the FLEUR and Wannier90 codes to construct the maximally-localized Wannier functions [31–33]. For all systems, the distance between the TM atoms and the rigid graphene layer was structurally optimized by total energy minimization neglecting SOC. We confirmed that the relaxations of the carbon atoms within the graphene layer are indeed very small, and neglecting them does not lead to any changes in the calculated quantities. TMs bond covalently with graphene [21], thus we suspect that the van der Waals interaction plays a minor role.

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